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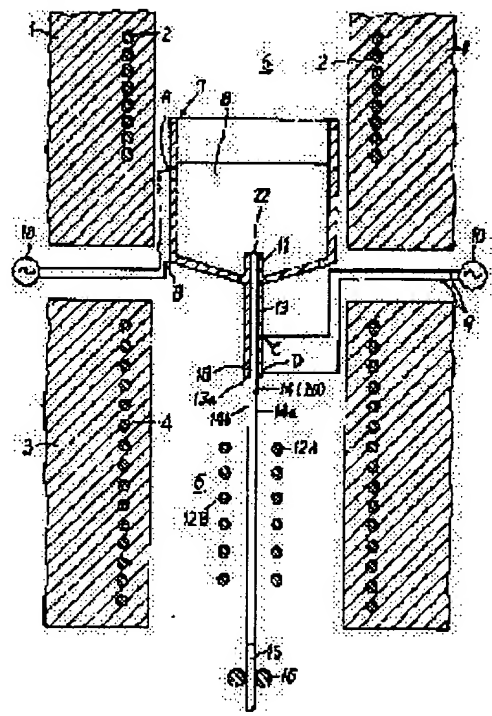
(71)Applicant : NGK INSULATORS LTD
(72)Inventor : IMAEDA MINORU
IMAI KATSUHIRO
HONDA AKIHIKO

(54) GROWING OF SINGLE CRYSTAL AND DEVICE THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To eliminate the need for forming a single crystal after growth to a single domain by growing the single crystal formed as the single domain at the time of continuously growing the single crystal by a micro-pulling down method.

SOLUTION: The single crystal 14 is formed by cooling the melt of a single crystal material while this material is pulled down from a crucible 7. The single crystal 14 is provided with a temp. gradient near the Curie temp. in the cooling process of the single crystal 14, by which the single crystal is pulled down and the single domain is continuously formed. The device is provided with temp. control mechanisms 12A, 12B for providing the single crystal 14 with the temp. gradient near the Curie temp.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the training method of the single crystal by the micro reduction method, and its equipment.
[0002]
[Description of the Prior Art] Recently, the method of forming a single crystal fiber by the so-called micro reduction method attracts attention as a method of raising an oxide single crystal. The circumstances where single crystal fibers, such as a niobic acid and a potassium lithium (it is indicated as KLN K3 Li2-2xNb5+x O 15+x and the following.), were raised by this method are indicated by 4-8 pages of the "Electrotechnical Laboratory news" July, 1993 issue (No. 522), JP,4-280891,A, and JP,6-345588,A.
[0003] According to the aforementioned report of the "Electrotechnical Laboratory news", resistance heating of the power is supplied and carried out to the cell or crucible made from platinum. The outlet of melting liquid is formed in the pars basilaris ossis occipitalis of this cell, the rod-like structure called melt feeder into this outlet is inserted in, and both the amount of supply to the outlet of melting liquid and the state of a solid phase liquid phase interface are controlled by this. The narrow diameter KLN single crystal fiber is continuously formed by adjusting the aperture of a melting liquid outlet, the size of a feeder, the wire extension of the feeder from an outlet, etc. According to this mu reduction method, a single crystal fiber with a diameter of 1mm or less can be formed, reduction of heat distortion, control of the convection current in melting liquid, and the diameter of a single crystal fiber can be controlled easily, and it has the feature that the small quality single crystal suitable for especially blue second harmonic generations is producible. Moreover, it is similarly used for the device for blue second harmonic generations, the waveguide device for optical communication, and surface-acoustic-wave-filter devices. LiNbO3 and LiTaO3 etc. -- ******** -- it is known that it can raise
[0004] Moreover, in the single crystal growth in a micro reduction method, in order to suppress generating of the cooling crack by the distortion immediately after training etc. conventionally about the process which cools the raised crystal, considering the temperature controls (a temperature gradient, annealing, etc.) of the near as a raising point is examined.
[0005]
[Problem(s) to be Solved by the Invention] However, when the single crystal fiber which consists of a ferroelectric compound like LiNbO3, LiTaO3, and KLN, for example was raised, it became clear that the obtained single crystal fiber probably serves as region structure, or become single domain structure by chance, and a result with sufficient repeatability is not obtained. When the second-harmonic (SHG) generating element was manufactured using such a single crystal fiber and the SHG generating efficiency etc. was evaluated, efficiency big on the whole was not acquired. For this reason, it was indispensable to have carried out single domain processing of the once raised single crystal separately.
[0006] However, in order to perform single domain processing to a ferroelectric single crystal, it is required to make the powder of LiNbO3, LiTaO3, and KLN carry, and to impress voltage by the

platinum board electrode. Degradation arises in the crystallinity of a single crystal between this single domain-ized processing. Moreover, depending on the conditions when impressing voltage, the damage of a crack etc. occurring is in a single crystal. Furthermore, it is necessary to carry out the process for complicated single domain-ized processing, and the whole manufacturing installation also becomes complicated.
[0007] The technical problem of this invention is enabling it to raise the single crystal which formed the single crystal into the single domain on the occasion of raising continuously by the micro reduction method, and is abolishing the need of forming the single crystal after training into a single domain by this. Moreover, it is that the crystalline good single crystal formed into the single domain is extremely obtained by this.
[0008]
[Means for Solving the Problem] this invention is the training method of a single crystal of cooling and making a single crystal generating, reducing the melt of single crystal material from a crucible, is the cooling process of the aforementioned single crystal, and relates to the training method of a single crystal characterized by making a single domain form continuously with pulling down the aforementioned single crystal by preparing a temperature gradient in the aforementioned single crystal in near the Curie point.
[0009] Moreover, this invention is training equipment of a single crystal equipped with the crucible equipped with the outlet for holding the melt of single crystal material and reducing a melt, the heating mechanism for carrying out melting of the aforementioned single crystal material in a crucible, and the drive for pulling down a single crystal from this crucible, and relates to the training equipment of a single crystal characterized by to have the heating mechanism for preparing a temperature gradient in a single crystal in near the Curie point.
[0010] this invention person has conducted the experiment which raises single crystal fibers, such as LiNbO3, LiTaO3, and KLN, by the micro reduction method, and the experiment for raising continuously single crystal plates, such as LiNbO3, LiTaO3, and KLN, by the micro reduction method, as further indicated in JP,8-259375,A. In the process of this research, it discovered that the interior of a single crystal fiber or a plate probably region-ized, or formed almost into a single domain, and the domain structure was not fixed even if it experiments by fixing manufacture conditions.
[0011] The idea that are the process which the melt reduced from the outlet of a crucible is cooled, solidifies, and is further reduced below although research was repeated for this invention person to trace this cause, and it was because the temperature around a single crystal is not fixed in especially this temperature field although Curie temperature is passed was obtained. That is, when a certain amount of temperature gradient had occurred in the single crystal at this time, what single domain-ization advances according to this temperature gradient, domain structure generates at random when there are few temperature gradients in the interior of single crystal or they do not exist, and region structure probably generates was presumed.
[0012] When the heating mechanism was controlled by conditions which a temperature gradient actually produces in a single crystal at least in the neighborhood of Curie temperature based on this presumption, the single crystal was always fixed, discovered forming a single domain, and reached this invention.
[0013] Specifically, in order to control the temperature gradient inside single crystal itself, when making it the temperature gradient of both sides of the single crystal in the state where it is reduced become 10 degrees C or more, it found out that it was stabilized and the single crystal of single domain structure could be raised. That is, it found out that the single crystal of the single domain structure where a low temperature side is [an elevated-temperature side] a plus side in respect of minus was obtained by controlling the temperature gradient near the Curie point to give a temperature gradient 10 degrees C or more to both sides, such as a raised single crystal plate. It is desirable to make this temperature gradient into 50 degrees C or more further from this viewpoint.
[0014] On the other hand, crystalline degradation by the stress inside a single crystal and generating of a crack can be prevented by making this temperature gradient into 300 degrees C or less. In order to raise the crystallinity of a single crystal further from this viewpoint, it is desirable to make this temperature

gradient into 200 degrees C or less.

[0015]

[Embodiments of the Invention] The method and equipment of this invention are applicable to the both sides of a fiber-like single crystal and a plate-like single crystal. However, the single crystal of the shape of a tabular or a plate was running much more certainly [the formation of a single domain] rather than the fiber-like single crystal. Specifically, under predetermined conditions, both sides of the raised single crystal plate had still higher certainty and reliability, and polarization and the bird clapper of minus were found.

[0016] this invention is especially suitable when manufacturing a solid-solution single crystal. As a solid-solution single crystal, for example LiNbO3 and LiTaO3, Li(Nb, Ta) O3, KLN (K3 Li2-2xNb5+x O 15+x), KLTN[K3 Li2-2x(Tay Nb1-y)5+x O15+x] Ba1-X SrX Nb 2O6 The structure of the tungsten bronze made into the center can be illustrated.

[0017] LiNbO3, LiTaO3, and the KLN single crystal attract attention as an optical material, and attract attention especially recently as a single crystal for the blue optical-second-harmonic-generation (SHG) elements for semiconductor laser. Since this can be generated to a 390nm ultraviolet radiation field, it is using the light of such short wavelength, and the broad application the object for optical disk memories, the object for medicine, the object for photochemistries, for [various] optical measurement, etc. is possible for it.

[0018] Moreover, this invention is applicable to training of an oxide single crystal which carries out a composition segregation. For example, LiNbO3 When it receives and it makes neodymium dissolve, and the segregation coefficient is not 1, only the neodymium of an amount fewer than the amount of the neodymium in composition of a melt enters into a single crystal. For example, within a melt, even if about 1.0-mol neodymium contains, only about 0.3 mols enter into a single crystal. However, the single crystal which has composition of a melt and the same composition can be manufactured, without causing a segregation by cooling a melt quickly by nozzle circles. This is YVO4 replaced by other laser single crystals, for example, YAG, Nd, Er, and Yb which were replaced by Nd, Er, and Yb. It can receive and apply.

[0019] In this invention, if the training method of a single crystal, especially an oxide single crystal is a micro reduction method, especially limitation will not be carried out. However, it is required to equip training equipment with the temperature-control mechanism for preparing a temperature gradient in a single crystal in near the Curie point. It is necessary to specifically carry out the temperature control in near the Curie point of such a single crystal within the limits of **150 degrees C of Curie points. Although such a temperature-control mechanism is not carried out, either, especially as for limitation, it can illustrate the following suitably from a viewpoint of mass-production nature.

[0020] (1) Form a heater in right and left of a single crystal plate in the cooling zone of the lower part of a training furnace, respectively. In each heater, the temperature gradient of each portion in the vertical direction of a heater is made into the structure which can be set up freely, respectively.

[0021] (2) Form a heater in right and left of a single crystal plate in the cooling zone of the lower part of a training furnace, respectively. And in one field side of a single crystal, temperature by the side of one field of a single crystal is made higher 10 degrees C or more than the temperature by the side of the field of another side of this and an opposite side by forming a space heater in the outside of this heater, and making a space heater generate heat.

[0022] (3) Form a heater in right and left of a single crystal plate in the cooling zone of the lower part of a training furnace, respectively. The interval by the side of one field of a heater and a single crystal is relatively made small, and a heater and a single crystal are brought close. With this, the interval by the side of the field of another side of a heater and a single crystal is enlarged relatively, and a heater and a single crystal are kept away. By this, temperature by the side of one field of a single crystal is made higher 10 degrees C or more than the temperature by the side of the field of another side of this and an opposite side.

[0023] In addition, also in the case of a single crystal fiber, the method of (1) - (3) is employable.

[0024]

[Example] Hereafter, the example of this invention is explained still in detail, referring to a drawing. Drawing 1 is the outline cross section showing the manufacturing installation for single crystal growths.
[0025] The crucible 7 is installed in the interior of a furnace body. The top furnace 1 is installed and the heater 2 is laid underground in the top furnace 1 so that a crucible 7 and its top space 5 may be surrounded. The nozzle section 13 is prolonged toward down from the soffit section of a crucible 7, and outlet 13a is formed in the soffit section of the nozzle section 13. The bottom furnace 3 is installed so that the nozzle section 13 and the space 6 of the circumference may be surrounded, and the heater 4 is laid underground in the bottom furnace 3. A crucible 7 and the nozzle section 13 are all formed of a corrosion resistance conductive material. A heating furnace can also be divided into three or more zones, although various the gestalt of this heating furnace itself can be changed, for example, the heating furnace is divided into two zones in drawing 1 of course.
[0026] To the position A of a crucible 7, one electrode of a power supply 10 is connected by the electric wire 9, and the electrode of another side of a power supply 10 is connected to the soffit B of a crucible 7. To the position C of the nozzle section 13, one electrode of a power supply 10 is connected by the electric wire 9, and the electrode of another side is connected to the soffit D of the nozzle section 13. It dissociates, and each of these energization mechanisms of both are constituted so that the voltage can be controlled independently.
[0027] Within the crucible 7, the introduction pipe 11 is prolonged toward above and intake 22 is formed in the upper limit of this introduction pipe 11. This intake 22 is projected a little from the pars basilaris ossis occipitalis of a melt 8. The intake of this melt can also be formed in the bottom of a crucible so that it may not project from the pars basilaris ossis occipitalis of a crucible. In this case, the introduction pipe 11 is not formed. An interval can be kept and an after heater can be formed in space 6 so that the nozzle section 13 may be surrounded.
[0028] The temperature distribution of space 5 and 6 are defined appropriately, the raw material of a melt is supplied in a crucible 7, and power is supplied and is made to make the top furnace 1, the bottom furnace 3, and an after heater generate heat, and to generate heat in a crucible 7 and the nozzle section 13. In this state, in the single-crystal-growth section 18 in the soffit section of the nozzle section 13, a melt projects slightly from opening 13a, it is held with the surface tension, and the front face flat in comparison is formed.
[0029] Consequently, the single crystal plate 14 is continuously formed in the seed crystal 15 bottom, and it is pulled out toward down. In this example, this seed crystal 15 and the single crystal plate 14 are sent with the roller 16.
[0030] Although the single crystal plate 14 is cooled along with going downward from the nozzle section 13, in this example, Heaters 12A and 12B are further installed in the both sides of the single crystal plate 14. Usually, less than **200 degrees C of Curie temperature, the temperature of the single crystal plate 14 while passing through this field is set up so that it may become less than 150 degrees C preferably. A temperature gradient with one fields 14a and 14b of a single crystal 14 is adjusted as mentioned above by controlling each temperature of each heaters 12A and 12B.
[0031] Drawing 2 (a) is the side elevation of this single crystal 14, and drawing 2 (b) is a plan. This plate 14 is raised where a single domain is formed for example, in the direction of arrow E.
[0032] In addition, when the single crystal fiber 20 is made to raise in drawing 1, as shown in drawing 2 (c), a single domain is formed in the direction of arrow E within a fiber 20.
[0033] Drawing 3 is the outline cross section showing the manufacturing installation concerning other examples roughly. The same sign is attached to the same portion as the equipment of drawing 1, and the explanation is omitted. Moreover, the amount of [which is called the top furnace and bottom furnace which were shown in drawing 1] periphery omitted illustration in drawing 3. In the equipment of drawing 3, to the upper limit F of a crucible 7, and the abbreviation center section G, the electrode of power supply 10A is connected, to the abbreviation center section G and the soffit section H of a crucible 7, the electrode of power supply 10B is connected and the electrode of AC-power-supply 10C is connected to the upper-limit section I of the soffit section H of a crucible 7, and the nozzle section. AC-power-supply 10D is connected to the nozzle section 13. It dissociates, and each of these energization

mechanisms of both are constituted so that the voltage can be controlled independently.
[0034] Although the single crystal plate 14 is cooled along with going downward from the nozzle section 13, in this example, Heaters 12A and 12B are further installed in the both sides of the single crystal plate 14. Usually, less than **200 degrees C of Curie temperature, the temperature of the single crystal plate 14 while passing through this field is set up so that it may become less than 150 degrees C preferably. Furthermore, the space heater 19 is formed in the outside of heater 12A. A temperature gradient with one fields 14a and 14b of a single crystal 14 is adjusted as mentioned above by controlling each temperature of each heaters 12A, 12B, and 19.
[0035] Moreover, drawing 4 is the typical cross section showing the equipment concerning other examples of this invention, and attaches the same sign to the same member as the member shown in drawing 3 . Heaters 25A and 25B are installed in the both sides of the single crystal plate 14. Usually, less than **200 degrees C of Curie temperature, the temperature of the single crystal plate 14 while passing through this field is set up so that it may become 150 degrees C or less preferably. In one field 14a side of the single crystal plate 14, distance m of a plate 14 and heater 25A is relatively made small, and distance l of a plate 14 and heater 25B is relatively enlarged in the field 14b side of another side of a plate 14. By this, the temperature gradient of field 14a and field 14b can be adjusted in the fixed range.
[0036] Next, in order to manufacture a single crystal plate, especially the gestalt of the suitable nozzle section is explained. the flat side of the flat-surface configuration on mu reduction method and corresponding to [in this invention person] the cross section of a single crystal plate to the nose of cam of the nozzle section -- forming -- this nozzle section -- the melting physical distribution through-hole of two or more trains -- forming -- from each melting physical distribution through-hole -- simultaneous -- a melt -- reducing -- each circulation -- it checked that a single crystal plate could be formed by unifying the melt reduced from the hole along a flat side
[0037] The whole nozzle section can be made into a monotonous configuration in this mode. Moreover, the extended section can be prepared at the nose of cam of the tubular nozzle section, and the apical surface of this extended section can be made into the above flat sides. Or two or more tubular members can constitute the nozzle section, and each tubular member of each other can be joined, it can unify, and the flat side of one can be formed by the apical surface of each tubular member.
[0038]
[Example] Hereafter, a still more concrete experimental result is described. A single crystal manufacturing installation as shown in drawing 1 is used, this invention is followed, and it is $LiNbO_3$. The single crystal plate 14 was manufactured. The temperature in [whole] a furnace was controlled by the top furnace 1 and the bottom furnace 3. It constituted so that the temperature gradient of the single-crystal-growth section 18 neighborhood could be controlled by the electric power supply to the nozzle section 13, and generation of heat of an after heater. As a reduction mechanism of the single crystal plate 14, the mechanism in which the single crystal plate 14 was pulled down was carried perpendicularly, controlling reduction speed within the limits of 2-100mm/hour uniformly.
[0039] The lithium carbonate and the niobium oxide were prepared by the composition ratio of 50:50, and raw material powder was manufactured. About 50g of this raw material powder was supplied in the crucible 7 made from platinum, and this crucible 7 was installed in the predetermined position. The temperature of the space 5 in the top furnace 1 was adjusted to the range of 1250-1350 degrees C, and the raw material in a crucible 7 was dissolved. The temperature of the space 6 in the bottom furnace 3 was controlled at 700 degrees C - 1000 degrees C. Predetermined power was supplied to a crucible 7, the nozzle section 13, and the after heater, and single crystal growth was carried out. Under the present circumstances, temperature of the single-crystal-growth section could be made into 1200 degrees C - 1300 degrees C, and the temperature gradient in the single-crystal-growth section was able to be controlled [mm] in 10-150 degrees C /.
[0040] The configuration of the cross section of the outside of the nozzle section 13 was made into the rectangle, and the size was set to 1.0mmx30mm. The length of the nozzle section 13 was set to 20mm. 30 melting physical distribution through-holes were prepared in the nozzle section 13. The diameter of each melting physical distribution through-hole was set to 0.2mm. It presupposed that the flat-surface

configuration of a crucible 7 is circular, the diameter was set to 30mm, and the height was set to 30mm.
[0041] The temperature gradient with the fields 14a and 14b of the single crystal plate 14 was set as 50 degrees C. The single crystal plate with a width of face [of 50mm] and a thickness of 1.0mm was pulled down to a shaft orientations by 20mm/hour in speed. The 80mm cooling zone cooled from near 1150 degree C to near 1000 degree C was prepared, and this zone was passed over about 4 hours by 20mm/hour in training speed.
[0042] Moreover, this single crystal plate was decomposed thermally at 180 degrees C by 3:1 mixed liquor of a hydrofluoric acid and a nitric acid for 1 hour. Consequently, to the plus side not **********ing at all, about 10 micrometers **********s in the minus side, and the etch pit was accepted in the bad crystalline portion. Consequently, it checked that the crystal of a perfect single domain was obtained.
[0043] Moreover, this LiNbO3 When the SHG generating efficiency of a single crystal was measured, as compared with the single crystal which performed the conventional single domain-ized processing, it was improving about 30%. It is related that became small about 20% with half-value width as this cause, reduction in distortion, for example, an X-ray rocking curve, and crystallinity improved. [substrate]
[0044]
[Effect of the Invention] Like, according to this invention, the single crystal which formed the single crystal into the single domain on the occasion of raising [which was described above] continuously by the micro reduction method can be raised, and single domain-ized processing of the single crystal after training can be made unnecessary. The crystalline good single crystal formed into the single domain came to be extremely obtained by this.

[Translation done.]

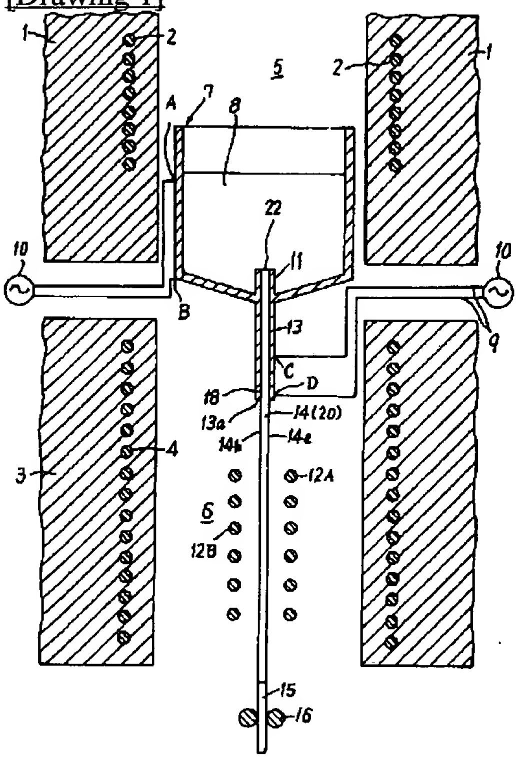
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the outline cross section concerning the example of this invention showing the manufacturing installation for single crystal growths.
[Drawing 2] (a) is the side elevation of the single crystal plate 14, (b) is the plan of the single crystal plate 14, and (c) is the cross section of the single crystal fiber 20.
[Drawing 3] It is the outline cross section showing the important section of the manufacturing installation for single crystal growths concerning other examples of this invention.
[Drawing 4] It is the outline cross section showing the important section of the manufacturing installation for single crystal growths concerning the example of further others of this invention.
[Description of Notations]
1 Top Furnace, 2 Seed Crystal, 18 Single-Crystal-Growth Section, 20 Single Crystal Fiber, 19 Space Heater, 25, and 25A Heater Heater of Top Furnace 1, 3 Bottom Furnace, 4 Heater of Bottom Furnace 3, 7 Crucible, 10, 10A, 10B, 10C, 10D Power Supply, 12A, 12B 2 Zone Heater, 13 Nozzle Section, 13a Outlet, 14 Single-Crystal Plate, 15

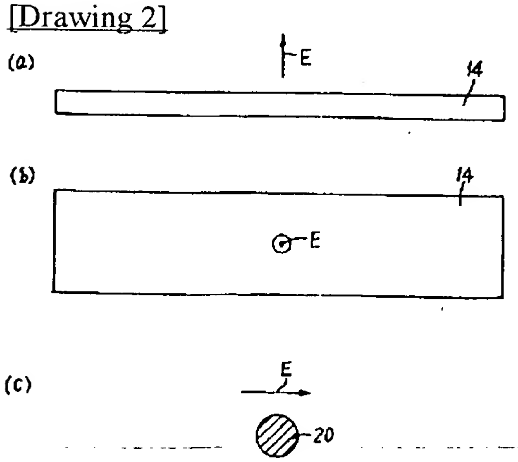
[Translation done.]

DRAWINGS

[Drawing 1]

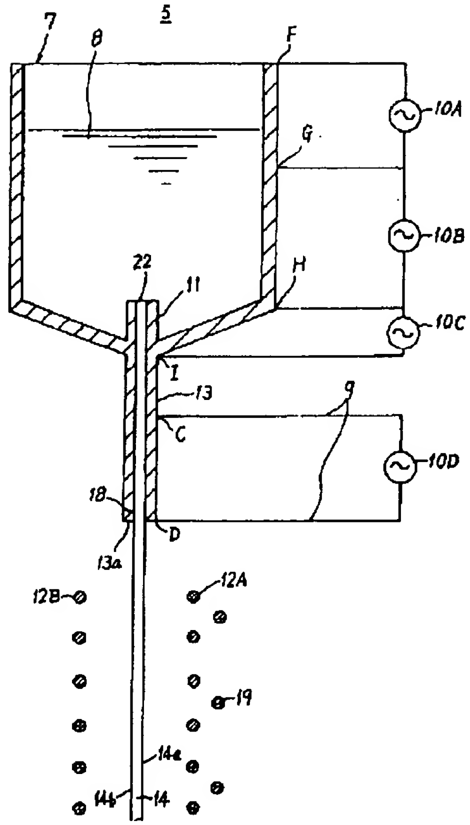


[Drawing 2]



[Drawing 3]

h g cg b eb cg e e



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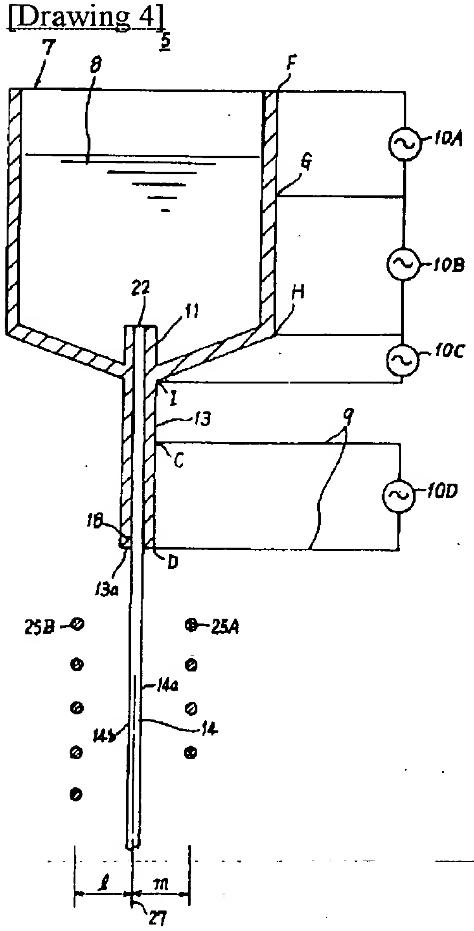
[Drawing 4]



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CLAIMS

[Claim(s)]
[Claim 1] The training method of a single crystal characterized by making a single domain form continuously with pulling down the aforementioned single crystal by being the training method of a single crystal of cooling and making a single crystal generating, and preparing a temperature gradient in the aforementioned single crystal in near the Curie point by the cooling process of the aforementioned single crystal, reducing the melt of single crystal material from a crucible.
[Claim 2] The training method of a single crystal according to claim 1 that the temperature gradient in the same reduction position of the aforementioned single crystal at the time of pulling down the aforementioned single crystal is characterized by being 10 degrees C - 300 degrees C.
[Claim 3] The training method of a single crystal according to claim 1 characterized by the aforementioned single crystal being a ferroelectric.
[Claim 4] The training equipment of a single crystal characterized by to have the temperature-control mechanism for being training equipment of a single crystal equipped with the crucible equipped with the outlet for holding the melt of single crystal material and reducing the aforementioned melt, the melting heating mechanism for carrying out melting of the aforementioned single crystal material in the aforementioned crucible, and the drive for pulling down the aforementioned single crystal from this crucible, and preparing a temperature gradient in the aforementioned single crystal in near the Curie point.

[Translation done.]